Statistical and Thermal Physics: Homework 16

Due: 20 April 2020

1 Thermodynamics of spin systems

Consider a system of N spin-1/2 particles, each with magnetic dipole moment μ and in a magnetic field of magnitude B. Let n_+ the number of particles with spin up.

a) Show that the temperature of the system satisfies

$$\frac{1}{T} = \frac{k}{2\mu B} \ln \left[\frac{N - E/\mu B}{N + E/\mu B} \right]$$

and use the result to determine an expression for the energy equation of state $E = E(T, N)$.

b) List the range of possible values of E and plot the temperature as a function of E over the entire range. Describe the range of energies for which the temperature is positive and that for which it is negative.

c) Using the probabilities with which a single particle is in the spin up state or the spin down state, determine the mean energy $\overline{E}$ for a single particle. How does this compare to the expression for the energy, E, of the entire system that you obtained earlier?

2 Spin system in equilibrium with an environment

Consider a system of N spin-1/2 particles, each with magnetic dipole moment μ and in a magnetic field of magnitude B. Suppose that the system is in equilibrium with an environment at temperature $T > 0$.

a) Explain whether the number of particles in the spin up state is larger than, smaller than or the same as the number in the spin down state.

b) Consider various spin systems in contact with environments at various temperatures. As the temperature of the environment increases does the fraction of particles in the spin up state increase, decrease or remain constant? Explain your answer.

3 Spin-1/2 particles in contact with an environment

Consider a system of N spin-1/2 particles, each with magnetic dipole moment μ and in a magnetic field of magnitude B. Suppose that the system is in equilibrium with an environment at temperature $T > 0$.

a) Consider a single particle in the ensemble. What temperature would guarantee that the particle is in the spin-up state with certainty? Explain your answer.

b) What temperature is such that the particle is equally likely to be in the spin up state versus in the spin down state? Explain your answer.

c) Nuclear magnetic resonance (NMR) uses such systems of spin-1/2 particles. In this case the signal provided by any particle with spin-up cancels that provided by any particle with spin down. In order to increase the signal strength would it be better to increase or decrease the temperature of the system? Explain your answer.

4 Einstein solid: high temperature limit

For an Einstein solid where $q \gg N$, we found that

$$\Omega(N,q) \approx \left(\frac{eq}{N}\right)^N \frac{1}{\sqrt{2\pi N}}.$$

Recall that the energy of the solid is

$$E = \hbar\omega \left(q + \frac{N}{2}\right).$$

a) Determine an expression for the temperature of the Einstein solid in terms of the total energy of the solid.

b) Use this to determine an expression for the energy equation of state of the solid $E = E(N,T)$. Does the energy have the expected behavior in terms of the number of particles?

c) Using $q \gg N$ show that the result of the previous part implies that $kT \gg \hbar\omega$ (this is why it is called the high temperature limit). Determine the approximate energy of one mole of such oscillators at a temperature of 300 K.

5 Einstein solid: low temperature limit

For any Einstein solid

$$\begin{aligned}\Omega(N,q) &\approx \left(1 + \frac{q}{N-1}\right)^{N-1} \left(1 + \frac{N-1}{q}\right)^q \sqrt{\frac{N+q-1}{2\pi(N-1)q}} \\ &\approx \left(1 + \frac{q}{N}\right)^N \left(1 + \frac{N}{q}\right)^q \sqrt{\frac{N+q}{2\pi N q}}\end{aligned}$$

whenever $q \gg 1$ and $N \gg 1$.

In the low temperature limit $q \ll N$.

a) Show that if $1 \ll q \ll N$ then

$$\Omega(N,q) \approx \left(\frac{eN}{q}\right)^q \frac{1}{\sqrt{2\pi q}}$$

and

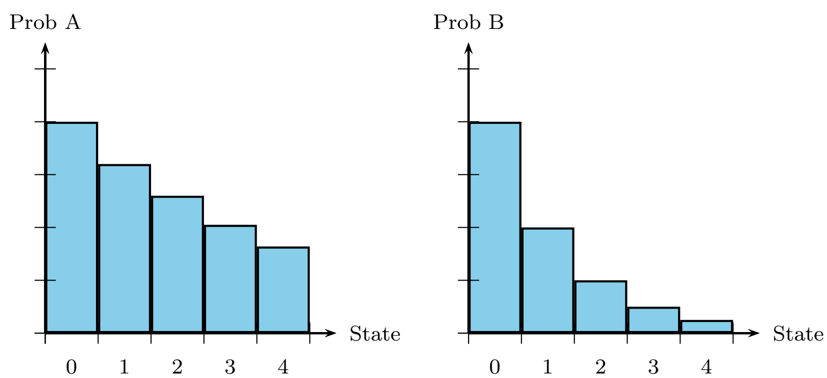
$$S = kq \left[\ln\left(\frac{N}{q}\right) + 1\right].$$

b) Use this to determine an expression for the temperature of the solid in terms of energy. Use this to get an expression for the energy in terms of temperature.

6 Gould and Tobochnik, *Statistical and Thermal Physics*, 4.24, page 210.

7 Energy distributions

Two collections of "toy model" molecules have the following energy distributions.



Which of these has the larger temperature? Explain your answer.

8 Five state system

Consider a particle which could be in one of five possible states; the energies of these states are $0, \epsilon, 2\epsilon, 3\epsilon$ and 4ϵ.

a) Suppose that $\epsilon = 0.050\,\mathrm{eV}$ and $T = 100\,\mathrm{K}$. Determine the probabilities with which the particle could be in each state and plot a bar graph of these.

b) Suppose that $\epsilon = 0.050\,\mathrm{eV}$ and $T = 500\,\mathrm{K}$. Determine the probabilities with which the particle could be in each state and plot a bar graph of these.

c) Suppose that $\epsilon = 0.20\,\mathrm{eV}$ and $T = 500\,\mathrm{K}$. Determine the probabilities with which the particle could be in each state and plot a bar graph of these.

d) Use your results to describe qualitatively the appearance of the entire bar graph as the temperature increases.

e) Use your results to describe qualitatively the appearance of the entire bar graph as the energy gap, ϵ, increases.

a) First relate energy to $n_+ =$ number spin up

$$E = -\mu B n_+ + \mu B n_- \quad \text{and} \quad n_- = N - n_+$$

$$\Rightarrow \quad E = \mu B (N - 2n_+) \qquad \Rightarrow \quad n_+ = \frac{1}{2}\left(N - \frac{E}{\mu B}\right)$$

Then $\frac{1}{T} = \frac{\partial S}{\partial E}$ and $S = k \ln[\Omega(E)]$ will give temperature

Here $\Omega = \binom{N}{n_+} = \frac{N!}{n_+!(N-n_+)!}$

$$S = k \ln \frac{N!}{n_+!(N-n_+)!} = k\left[\ln N! - \ln n_+! - \ln(N-n_+)!\right]$$

$$\approx k\left[N\ln N - \cancel{N} - n_+ \ln n_+ + \cancel{n_+} - (N-n_+)\ln(N-n_+) + N - n_+\right]$$

$$= k\left[N \ln N - (N-n_+)\ln(N-n_+) - n_+ \ln n_+\right]$$

Now $\frac{\partial S}{\partial E} = \frac{\partial S}{\partial n_+}\frac{\partial n_+}{\partial E} \quad \Rightarrow \quad \frac{1}{T} = \frac{\partial S}{\partial n_+}\left(\frac{-1}{2\mu B}\right)$

and $$\frac{\partial S}{\partial n_+} = k\left[-\ln n_+ - \cancel{n_+/n_+} + \ln(N-n_+) - \cancel{\frac{N-n_+}{N-n_+}(-1)}\right]$$

$$= -k\left[\ln n_+ - \ln(N-n_+)\right]$$

$$= -k \ln\left(\frac{n_+}{N-n_+}\right)$$

$$\Rightarrow \quad \frac{1}{T} = -k\ln\left(\frac{n_+}{N-n_+}\right)\left(-\frac{1}{2\mu B}\right)$$

$$\Rightarrow \quad \frac{1}{T} = \frac{k}{2\mu B}\ln\left(\frac{n_+}{N-n_+}\right)$$

Thus with $n_+ = \frac{1}{2}\left(N - \frac{E}{\mu B}\right)$

$$N - n_+ = \frac{1}{2}\left(N + \frac{E}{\mu B}\right)$$

we get

$$\frac{1}{T} = \frac{k}{2\mu B} \ln\left[\frac{N - E/\mu B}{N + E/\mu B}\right]$$

Alternative expressions are

$$\frac{1}{T} = \frac{k}{2\mu B} \ln\left(\frac{n_+}{N - n_+}\right) \qquad \frac{1}{T} = \frac{k}{2\mu B} \ln\left(\frac{n_+}{n_-}\right)$$

To invert this:

$$\frac{2\mu B}{kT} = \ln\left(\frac{N - E/\mu B}{N + E/\mu B}\right)$$

$$e^{2\mu B/kT} = \frac{N - E/\mu B}{N + E/\mu B} \Rightarrow Ne^{\cdots} + \frac{E}{\mu B} e^{\cdots} = N - E/\mu B$$

$$\Rightarrow \frac{E}{\mu B}\left(e^{\cdots} + 1\right) = N\left(1 - e^{\cdots}\right)$$

$$\Rightarrow \boxed{E = \mu B N \left(\frac{1 - e^{2\mu B/kT}}{1 + e^{2\mu B/kT}}\right)}$$

b) The range of n_+ is

$$0 \le n_+ \le N$$

Thus when $n_+ = 0$ $\quad E = \mu B N$

when $n_+ = N$ $\quad E = -\mu B N$

$$\Rightarrow -\mu B N \le E \le \mu B N$$

Now consider T as a function of E.

If $E \geq 0$ then $\quad \dfrac{N - E/\mu B}{N + E/\mu B} < 1 \Rightarrow \ln[\ldots] < 0 \Rightarrow T < 0$

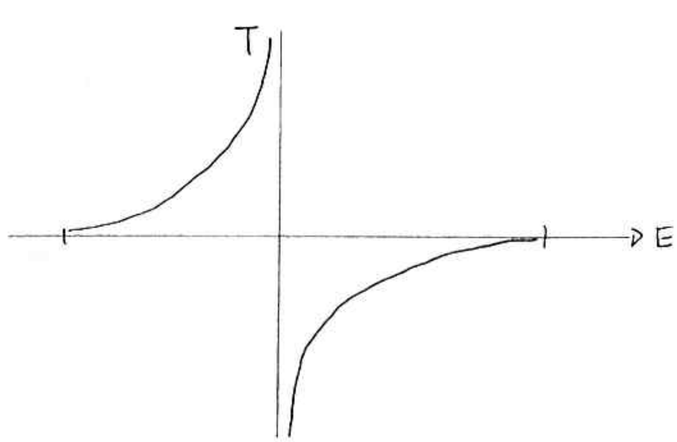
If $E \leq 0$ then $\quad \dfrac{N - E/\mu B}{N + E/\mu B} \geq 1 \Rightarrow \ln[\ldots] > 0 \Rightarrow T > 0$

Thus
$$\boxed{\begin{array}{l} \text{If } E \geq 0 \text{ then } T < 0 \\ \text{If } E \leq 0 \text{ then } T > 0 \end{array}}$$

Then as $E \to \mu B N$ $\quad \frac{1}{T} \to \frac{k}{2\mu B} \ln\left[\frac{0}{2N}\right] \to -\infty \to T \to 0$ from negative

as $E \to -\mu B N$ $\quad \frac{1}{T} \to \frac{k}{2\mu B} \ln\left[\frac{2N}{0}\right] \to \infty \to T \to 0$ from +ve.

as $E \to 0$ $\quad \frac{1}{T} \to 0 \Rightarrow T \to \pm\infty$



c) $$p_+ = \frac{1}{1+e^{-2\mu B/kT}} = \frac{e^{2\mu B/kT}}{e^{2\mu B/kT}+1}$$

$$p_- = \frac{e^{-2\mu B/kT}}{1+e^{-2\mu B/kT}} = \frac{1}{e^{2\mu B/kT}+1}$$

$$\bar{E} = E_+ p_+ + E_- p_-$$

$$= -\mu B\, p_+ + \mu B\, p_-$$

$$= \mu B \left[\frac{1}{e^{2\mu B/kT}+1} - \frac{e^{2\mu B/kT}}{e^{2\mu B/kT}+1}\right]$$

$$= \mu B \frac{1-e^{2\mu B/kT}}{1+e^{2\mu B/kT}}$$

Same as energy before with $N=1$.

The probabilities are

spin up $\quad p_+ = \dfrac{1}{1+e^{-2\mu B/kT}}$

spin down $\quad p_- = \dfrac{e^{-2\mu B/kT}}{1+e^{-2\mu B/kT}} = \dfrac{1}{1+e^{2\mu B/kT}}$

a) When $T>0$ $\quad e^{-\mu B/kT} < 1$

$\Rightarrow \quad 1+e^{-2\mu B/kT} < 2$

$\Rightarrow \quad p_+ > 1/2$

more in spin up

b) As T increases $\quad -\frac{2\mu B}{kT}$ increases $\Rightarrow \quad 1+e^{-2\mu B/kT}$ increases

$\Rightarrow \quad p_+$ decreases

fraction in spin up decreases

a) $$p_+ = \frac{1}{1+e^{-2\mu B/kT}}$$

we need $p_+ = 1 \Rightarrow e^{-2\mu B/kT} = 0$

$\Rightarrow \ln(-2\mu B/kT) = \underbrace{\ln(0)}_{-\infty}$

$\Rightarrow 2\mu B/kT = \infty$

$\Rightarrow T = 0$

We need $\boxed{T=0}$

b) we need $p_+ = 1/2 \Rightarrow e^{-2\mu B/kT} = 1$

$\Rightarrow \ln(e^{-2\mu B/kT}) = 1$

$\Rightarrow -2\mu B/kT = 0 \Rightarrow T = \infty$

We need $\boxed{T=\infty}$

c) Based on a,b) and need for p_+ to increase we need to decrease temperature

Phys 362

2020 HW 16 Q4

a) $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$ and we need

$$S = k \ln \Omega$$

$$\Rightarrow S = k \ln\left[\left(\frac{eq}{N}\right)^N \frac{1}{\sqrt{2\pi N}}\right]$$

$$S = k\ N\left[\ln e + \ln q - \ln N\right] - \frac{k}{2} \ln(2\pi N)$$

Then

$$\frac{\partial S}{\partial E} = \frac{\partial S}{\partial q}\frac{\partial q}{\partial E}$$

$$= \frac{Nk}{q}\frac{\partial q}{\partial E}$$

But $\quad q = \frac{E}{\hbar\omega} - N/2 \Rightarrow \frac{\partial q}{\partial E} = \frac{1}{\hbar\omega}$

So $\quad \frac{1}{T} = \frac{Nk}{q\hbar\omega} \Rightarrow T = \frac{\hbar\omega q}{Nk}$

Now $\quad E = \hbar\omega(q + N/2)$ and $q \gg N \Rightarrow E \cong \hbar\omega q$ Thus

$T = \frac{E}{Nk}$ $\quad$ $\left[\text{exact: } T = \frac{E - \frac{\hbar\omega}{2}N}{Nk}.\right]$

b) $\quad E = NkT$ $\quad$ $\left[\text{exact: } E = NkT + \frac{\hbar\omega}{2}N\right]$

Yes it is proportional to N

c) $E = NkT = \hbar\omega(q + N/2)$

$\approx \hbar\omega q$

$\Rightarrow \quad \frac{q}{N} \approx \frac{kT}{\hbar\omega} \gg 1$

Thus $kT \gg \hbar\omega$

$N = N_A = 6.02 \times 10^{23}$

$E = 6.02 \times 10^{23} \times 1.38 \times 10^{-23}\ J/K \times 300K$

$E = 2500J$

a) $\Omega \approx \left(1+\frac{q}{N}\right)^N \left(1+\frac{N}{q}\right)^q \sqrt{\frac{N+q}{2\pi N q}}$

If $1 \ll q \ll N$ then

$N+q \approx N$

$1+N/q \approx N/q$.

and

$$\Omega \approx \underbrace{\left(1+\frac{q}{N}\right)^N}_{\approx e^q} \left(\frac{N}{q}\right)^q \sqrt{\frac{\cancel{N}}{2\pi \cancel{N} q}}$$

$$\Rightarrow \quad \Omega = \left(\frac{eN}{q}\right)^q \frac{1}{\sqrt{2\pi q}}$$

Then $S = k\ln\Omega = k \ln\left[\left(\frac{eN}{q}\right)^q \frac{1}{\sqrt{2\pi q}}\right]$

$= k\left[\ln\left(\frac{eN}{q}\right)^q + k\ln\frac{1}{\sqrt{2\pi q}}\right]$

$= k\left[q\ln\left(\frac{eN}{q}\right) - \frac{k}{2}\ln(2\pi q)\right]$

$= k\left[q\left(\ln e + \ln\frac{N}{q}\right) - \frac{k}{2}\ln(2\pi q)\right]$

$= k\left[q\ln(N/q) + q - \frac{k}{2}\ln(2\pi q)\right]$

Then $q \gg \Rightarrow q \gg \ln(2\pi q)$ So

$$S \approx kq\left[\ln(N/q)+1\right]$$

b) $E = \hbar\omega(q + N/2) \Rightarrow q = \frac{E}{\hbar\omega} - \frac{N}{2}$

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

$$= \frac{\partial S}{\partial q}\frac{\partial q}{\partial E}$$

Then $\frac{\partial q}{\partial E} = \frac{1}{\hbar\omega}$

$$\frac{\partial S}{\partial q} = k\left[\ln\left(\frac{N}{q}\right) + 1\right] + \frac{kq}{N}\frac{q}{N}\left(-\frac{N}{q^2}\right)$$

$$= k\left[\ln\left(\frac{N}{q}\right) + 1 - 1\right]$$

$$= k\ln\left(\frac{N}{q}\right)$$

$$\Rightarrow \frac{1}{T} = \frac{k}{\hbar\omega}\ln\left(\frac{N}{q}\right) \Rightarrow T = \frac{\hbar\omega}{k}\Big/\ln\left(\frac{N}{q}\right)$$

$$= -\frac{\hbar\omega}{k}\Big/\ln\left(\frac{q}{N}\right) = -\frac{\hbar\omega}{k}\Big/\ln\left(\frac{E}{N\hbar\omega} - \frac{1}{2}\right)$$

$$T = -\frac{\hbar\omega}{k}\Big/\ln\left(\frac{E}{N\hbar\omega} - \frac{1}{2}\right)$$

Then $\ln\left(\frac{E}{N\hbar\omega} - \frac{1}{2}\right) = -\hbar\omega/kT$

$$\frac{E}{N\hbar\omega} - \frac{1}{2} = e^{-\hbar\omega/kT}$$

$$E = N\hbar\omega\left[e^{-\hbar\omega/kT} + \frac{1}{2}\right]$$

G+T Ch 4

Prob 4.24

The abundance can be determined by the probabilities. The fraction in state A is

$$f_A = p_A = \frac{e^{-E_A\beta}}{Z}$$

where E_A is the energy of state A. Let A = trans

B = cis.

Then

$$\frac{f_B}{f_A} = \frac{e^{-E_B\beta}}{Z} \Big/ \frac{e^{-E_A\beta}}{Z} = e^{-(E_B - E_A)\beta}$$

$$= e^{-\Delta E\beta} = e^{-4180K/T}$$

$T = 300K$ $\qquad \frac{f_B}{f_A} = e^{-\frac{4180}{300}} = 8.9\times10^{-7}$

$T = 1000K$ $\qquad \frac{f_B}{f_A} = e^{-\frac{4180}{1000}} = 0.015$

Then using N_A = # in trans state

N_B = # " cis state

$N_A = f_A N$ etc,... $\Rightarrow$

$$\boxed{\begin{array}{ll} \frac{N_B}{N_A} = 8.9\times10^{-7} & \text{at } 300K \\ \frac{N_B}{N_A} = 0.015 & \text{at } 1000K \end{array}}$$

2020 HW16 Q3

$$p_s = \frac{e^{-E_s\beta}}{Z}$$

Consider successive probabilities:

$$\frac{p_{s+1}}{p_s} = e^{-(E_{s+1}-E_s)\beta}$$

The drop in probability is larger when $(E_{s+1}-E_s)\beta$ is larger So the drop is larger when β is larger But $\beta = 1/kT$ implies.

larger drop $\Rightarrow$ smaller temp.

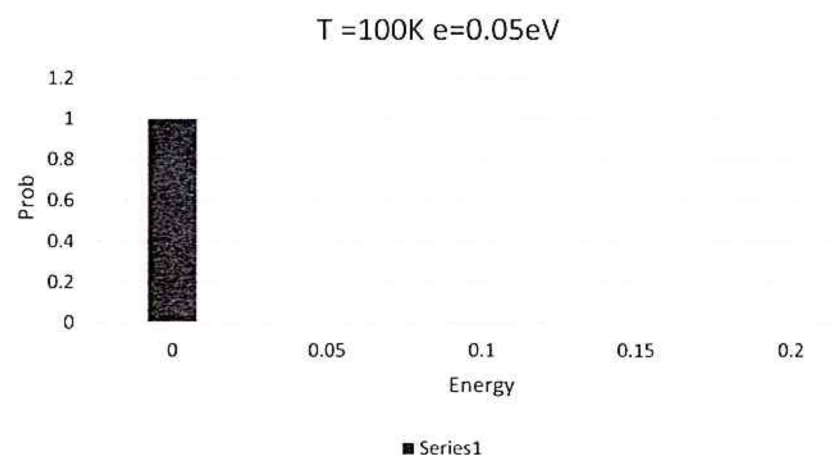
2020 HW 16 Q4a

k= 8.62E-05 epsilon= 0.05

T= 1.00E+02

state	energy	Boltzmann factor	prob
0	0	1	0.99698
1	0.05	0.003020045	0.003011
2	0.1	9.12067E-06	9.09E-06
3	0.15	2.75448E-08	2.75E-08
4	0.2	8.31867E-11	8.29E-11

Z= 1.003029194



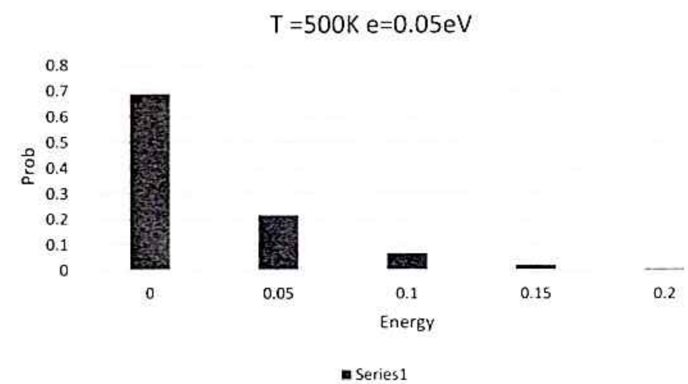
2019 HW 19 Q4b

k= 8.62E-05 epsilon= 0.05

T= 5.00E+02

state	energy	Boltzmann factor	prob
0	0	1	0.68875
1	0.05	0.313330513	0.215806
2	0.1	0.098176011	0.067619
3	0.15	0.03076154	0.021187
4	0.2	0.009638529	0.006639

Z= 1.451906593

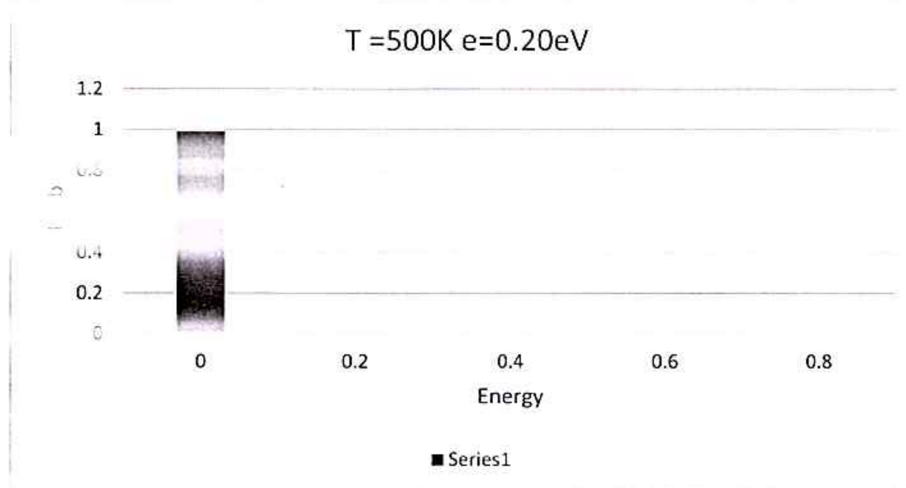


k= 8.62E-05 epsilon= 0.2

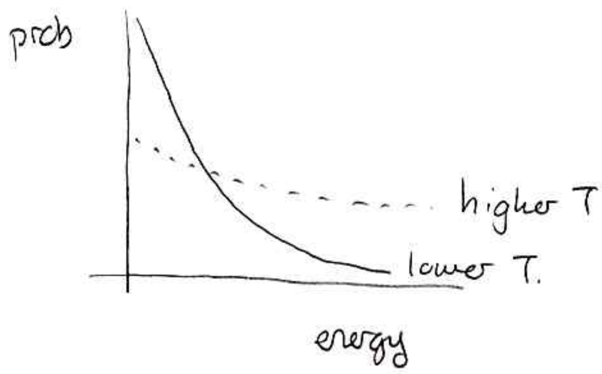
T= 5.00E+02

state	energy	Boltzmann factor	prob
0	0	1	0.990361
1	0.2	0.009638529	0.009546
2	0.4	9.29012E-05	9.2E-05
3	0.6	8.95431E-07	8.87E-07
4	[illegible]	[illegible]	[illegible]

Z= 1.009732334



d) The higher energy states become more probable



e) The lower energy states become more probable